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**PRESSURE-VOLUME RELATIONS FOR SEVENTEEN
ELEMENTS TO 100,000 kg/cm²**

By P. W. BRIDGMAN

**INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WITH AID FROM THE
RUMFORD FUND.**

(Continued from page three of cover)

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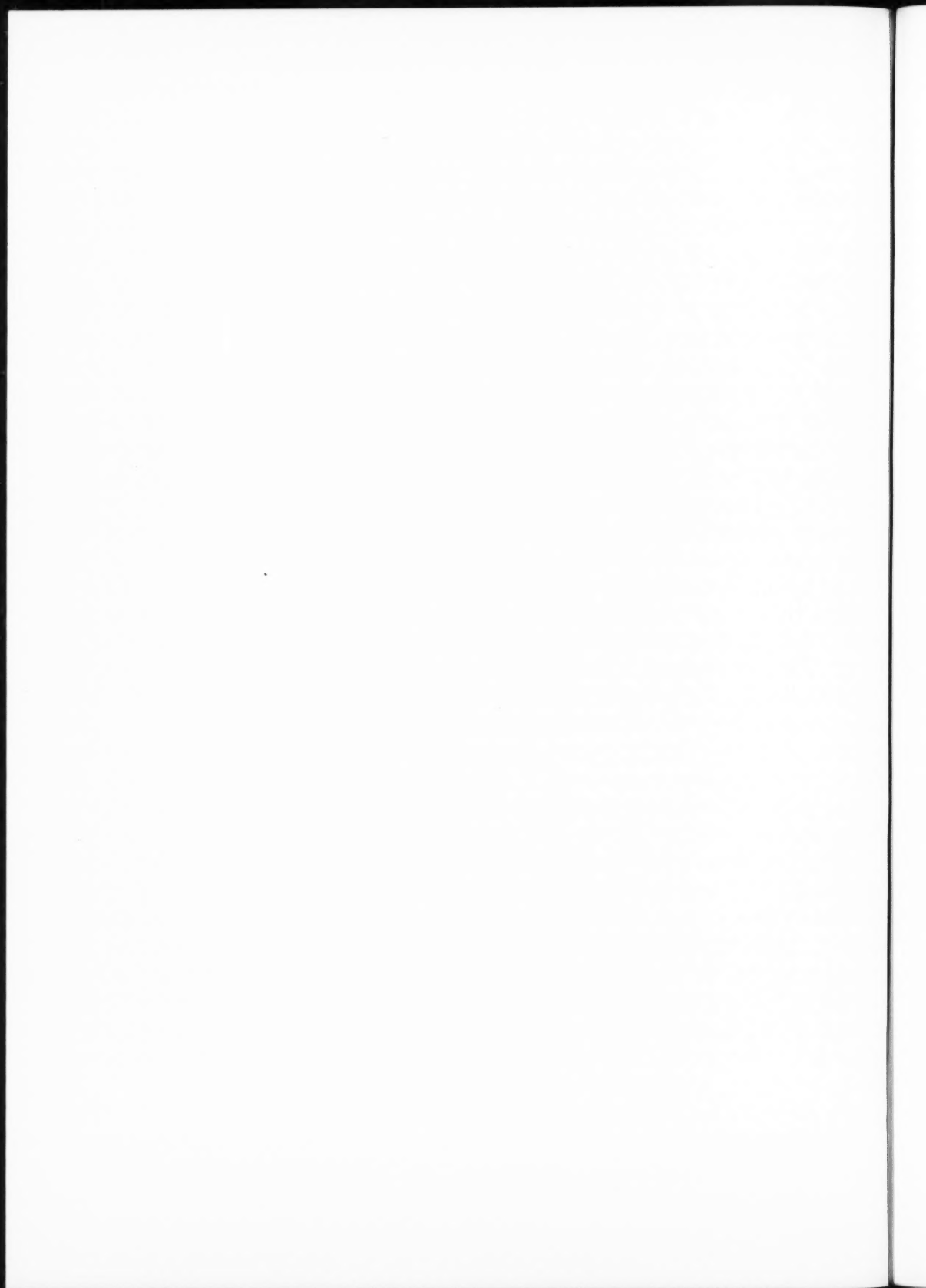
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INTRODUCTION AND GENERAL METHOD

This paper describes the first results of measurements above 50,000 kg/cm² in which the high pressure vessel is itself completely immersed in a liquid subjected to a pressure which in these experiments ranged from 25,000 to 30,000 kg/cm². A brief preliminary notice of the method has already been given.¹ The advantage of supporting the high pressure vessel with a liquid under pressure is two-fold: the maximum pressure is extended by the pressure of the liquid, and the intrinsic strength of the materials of the high pressure vessel is increased by the supporting pressure beyond the normal value. This increase of strength, however, is not as great as at first appeared, as I have already discussed in another paper,² and furthermore, when accurate measurements are in question it is not possible to utilize all the potential increase of strength, because of the slow plastic flow which appears to be the accompaniment of such increase of strength as there is at the higher supporting pressures. The limit of these measurements, 100,000 kg/cm², was set by considerations of accuracy limited by plastic flow, and also by economy, the life of a vessel diminishing rapidly as the range is increased.

In broad outline the method is as follows. The material whose compression is to be determined is placed in a small high pressure piezometer, which consists of a small cylinder with pistons projecting from either end. This piezometer is placed inside the apparatus for 30,000 kg/cm² with which a number of measurements have already been made and which has been described in detail.³ Pressure in the 30,000 apparatus is at first increased in the normal way by the advance of its piston. The various dimensions are so chosen that when the pressure in the 30,000 apparatus has reached approximately 25,000 its piston makes up on the pistons of the high pressure piezometer. Further advance of the piston

of the 30,000 apparatus increases the pressure within the high pressure piezometer by much more than the increase in the liquid of the 30,000 apparatus because of the small volume within the high pressure piezometer. The proportions are so chosen that pressure within the high pressure piezometer reaches 100,000 kg/cm² when the pressure in the 30,000 apparatus has increased from 25,000 to something between 27,000 and 30,000, depending on the material. I gave up the device of maintaining pressure in the confining liquid constant by bismuth in transition, the present method being more convenient and sufficiently accurate.

The pressure within the high pressure piezometer is obtained from a measurement of the extra force on the high pressure piston given by an electrical device completely immersed in the surrounding liquid; this device will be described presently. The displacement of the high pressure piston is obtained from the measured displacement of the piston of the 30,000 apparatus. Error from distortion of various parts of the apparatus is eliminated by making the method differential, taking the difference of displacement for the material under investigation and some standard substance of such small compressibility that its value at high pressures may be safely assumed from an extrapolation of its values at lower pressures. The method is not accurate, therefore, for substances of too low compressibility. The result of the measurements, after various corrections have been applied, is the volume as a function of pressure from a zero set by the pressure in the confining liquid, about 25,000 kg/cm². Both normal volume compressions and volume changes due to polymorphic transitions are thus obtained; the latter are distinguishable from the former by their discontinuity. The measurements have to be supplemented by others below 25,000. The materials selected for measurement in the following include most of the metallic elements with sufficiently large volume changes to give acceptable accuracy.

DETAILS OF THE APPARATUS

The heart of the apparatus is of course the piezometer. At first I used vessels of heat treated alloy steels. It appears to be possible to reach 100,000 (75,000 differential) with these without rupture or too great permanent set, but the accuracy obtainable is low because of slow plastic flow and very large distortion, more than 10 per cent on the cross section, with resulting irregularities from hysteresis. A paper by Basset⁴ gave me the idea that it might be possible to use containers of carboloy. I had previously

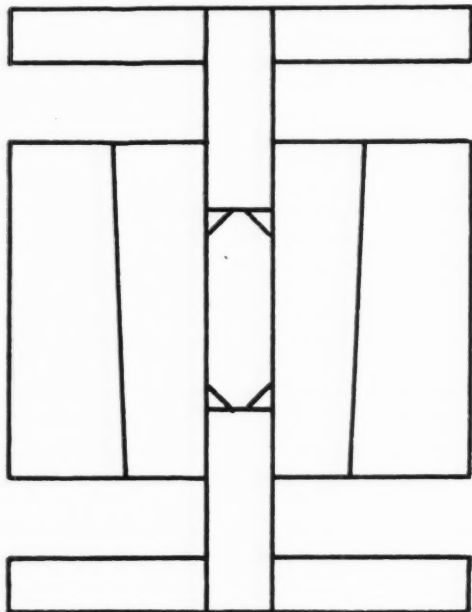


FIG. 1. The piezometer, consisting of a core of carboloy forced into a conical steel sleeve.

rejected this idea, both because of the mechanical difficulty of drilling long accurate holes in carboloy, and because of my fear that carboloy containers would rupture under internal pressure, carboloy normally being notably less strong than steel in tension and breaking with a brittle fracture in striking contrast to its much greater strength in compression. However, it appeared that Basset had used carboloy cylinders with external shrunk-on steel sleeves to support high internal pressure. One obvious great advantage of carboloy compared with steel is the much smaller elastic distortion, the elastic constants of

carboloy being about three times greater than those of steel. It furthermore appeared on inquiry that the technique exists for drilling accurate holes in carboloy. Holes 0.31 inch long, 0.0625 inch in diameter, accurate to 0.0001 inch, have been made for me both by the Carboloy Co. and by Mr. Fred White.

The piezometer is shown in Figure 1. The hole is first drilled in a suitable carboloy cylinder, which is then mounted on an arbor and the outside ground to a slight taper true with the hole. The tapered carboloy cylinder is then forced into a tapered external sleeve of heat-treated alloy steel in order to strengthen the carboloy to resist internal pressure by thus subjecting it to an initial compression. The taper used was about 0.004 inch in the length of the carboloy, and the amount of compression was sufficient to expand the steel by 0.002 inch. Under this compression the internal hole in the carboloy diminishes perceptibly, by something of the order of 0.0001 or 0.0002 inch. The amount of expansion which the steel will safely stand must be determined by trial. If the steel is too hard it may split off the carboloy core after standing for some time and after everything appears to be safely consummated. The brittleness of the carboloy in extension is shown by the fact that when the carboloy suddenly expands under the release of compression by the steel it may fly to pieces by its own inertia; I lost two carboloy cylinders in this way. With the dimensions shown the initial compression afforded by the steel sleeve probably did not rise above 15,000 kg/cm² and may well have been smaller. When immersed in the supporting liquid an additional compression results from the differential compressibility of steel and carboloy, but this effect amounts to the equivalent of only 2,000 or 3,000 kg/cm² at the maximum confining pressure. At the maximum internal pressure of 100,000 the carboloy is thus under a total compression of perhaps 45,000, 25,000 arising from the liquid and the balance from the steel ring, leaving 55,000 tension on the inside. Under normal conditions carboloy would break at a tension of less than half of this; that it is able to support it under these conditions must be an effect of the confining pressure.

Four piezometers have been used in this work, of different grades of carboloy. Two were of grade no. 905. The first of these broke after eleven exposures to about 100,000 and ten other exposures to from 80,000 to 90,000. The final rupture occurred with a filling of lithium, allowed

to come directly in contact with the carboly without protection, and at the time was ascribed to chemical action between lithium and carboly, in analogy with the known chemical action under high pressure of sodium and steel. The conclusion was not checked, however, and in view of the life of the other piezometer of the same grade of carboly, the natural life of the piezometer may have been reached and the connection with chemical action may have been only apparent. The second piezometer of no. 905 broke after seventeen applications of 100,000 or more; the final rupture occurred with a filling of indium, which is known not to exert any chemical effect on steel, at least in the range up to 50,000, and probably not to 100,000, because previously a successful run had been made with indium up to 100,000. A third piezometer of carboly grade no. 779 ruptured on the second application of 100,000. The initial filling had been with arsenic, with no protection, and significance was ascribed to this, although again there was no check. The fourth piezometer of grade no. 55A has withstood sixteen applications of 100,000 or more, and is not ruptured at this writing. A considerably longer life was anticipated for grade no. 55A because at atmospheric pressure it is materially stronger in tension than no. 905.

These carboly piezometers take a very small amount of set internally after exposure to pressure; the set can be detected delicately with the fingers in a greater looseness of the carboly pistons, but is so small as to introduce no appreciable error, and does not appear to increase perceptibly as a prelude to rupture. The rupture may take the form of minute fissures permeating the mass of carboly, but not penetrating through to the outside. After the rupture of the piezometer with indium little sheets and worms of indium continued to ooze slowly out of the inner wall of the piezometer for half a day.

The pistons of carboly were forced into supporting discs of steel as shown; this both increases the strength of the pistons by supporting the ends and increases the accuracy of centering and alignment. The initial diameter of the piston was made about 0.0002 inch less than that of the hole. At the top pressure the pistons almost always received some shortening with corresponding increase of diameter. This plastic flow occurs over a wide range before rupture with slowly increasing velocity as the rupture point is approached. The result is that the force applicable to the pistons is much less when accurate

measurements are demanded than the maximum possible on a quick application of pressure without rupture. Thus when pressure is rapidly applied up to the rupture point in compression I have measured² strengths ranging from 125,000 to 150,000 kg/cm², but under the slow increase of pressure required when measurements with the piezometer are made the shortening and consequent increase of cross section is already so great at 110,000 as to produce unpleasantly large friction of the piston in the piezometer. Carboly differs from steel not only in its greater range of plastic flow, but also in its smaller work hardening; the pistons did not accommodate themselves to the maximum, but on every new set-up there was additional set after exposure to the maximum, and this did not tend to diminish markedly with repetition. After every excursion it might be necessary to reduce the diameter of the piston to its initial value by removing perhaps 0.0002 inch with fine diamond powder. The maximum permanent shortening in any of the following measurements was 0.004 inch on a total length of 0.3 inch; it usually fluctuated between 0.001 and 0.002. Most of the work was done with pistons of grade no. 905. Toward the end, however, grade no. 999, which has a smaller amount of cobalt, was tried, with much improved results from the point of view of permanent set. It does not appear, however, that the ultimate compressive strength of no. 999 is materially higher than that of no. 905; it is merely that it is more brittle and the plastic flow is slower. After a number of redressings the pistons become too much out of round and must be discarded. The life of the piston does not average more than half that of the piezometer.

The contents of the piezometer were prevented from leaking past the pistons by small conical packing rings as indicated. These are made of heat-treated alloy steel, drawn back far enough to be machinable in the lathe. The rings are made initially a drive fit for the piezometer. It was a gratification that there was not more difficulty from leak past the pistons, which I had feared. There was trouble from leak only once or twice and that with the softest materials. If the piston is made too small for the hole, the packing rings will crowd into the annular space between piston and piezometer wall, very much increasing the friction. As already mentioned, an initial clearance of about 0.0001 inch proved satisfactory. At the maximum pressure this clearance approximately doubles at the working

end of the piston. The expansion of the bore of the piezometer is partly compensated by the expansion of the piston under compression.

There are two advantages in making the piezometer double ended with two pistons. Filling and emptying are much facilitated. Since the pistons move freely from each end, the effective length of the charge of the piezometer is halved. This reduces the frictional resistance to motion of the pistons arising from drag of the charge on the walls of the piezometer, which has the result of making the effective pressure at the center of the piezometer less than under the advancing end of the piston. Since the total frictional drag increases exponentially with increase of length of the piezometer, halving the length decreases the friction to less than one half.

The force with which the pistons are pushed into the piezometer by the advancing piston of the 30,000 apparatus is determined from the change of electrical resistance of a "compressometer." This has already been briefly described.² It consists of a cylindrical sleeve of heat-treated alloy steel cut longitudinally alternately from the two ends into a grid which offers a comparatively long path to the flow of current. The electrical resistance is measured on a potentiometer by methods previously extensively used and described in my work to 30,000. The electrical resistance changes by a certain fractional amount for a given intensity of compressive stress in the walls of the compressometer. Within limits set by feasibility of construction and mechanical stability the absolute resistance of the compressometer may be given any desired value for a given total compressive strength. Some little preliminary work was done in finding a suitable steel. Some grades of steel show hysteresis in the resistance as a function of compressive stress. The steel finally adopted was "Teton" steel of the Carpenter Steel Co., quenched into oil from 870° C. and drawn to 200° C. Compressometers of several different dimensions have been used for various purposes, depending on the total compressive force necessary to transmit. Two compressometers were used in this work, the first being ruptured by an explosion. The dimensions of these were approximately: length 0.29 inches, outside diameter 0.44 inches, wall thickness 0.032 inches, and resistance 0.045 ohms. The calibration of the compressometer will be described later.

The hydrostatic pressure in the supporting liquid was measured with a manganin resistance

gauge, calibrated and manipulated as has been described in a recent paper.⁵ The gauge demands one insulated lead and the compressometer three, thus demanding an insulating plug with four terminals. Gauge and compressometer were grounded to the cylinder of the 30,000 apparatus. In the early work with the 30,000 apparatus the insulated leads proved a major difficulty, not being able at first to stand more than two applications of pressure. In my last paper on measurements to 30,000 the use of a new design for insulating the stems was reported which appeared promising. This has been used in all this present work, with minor changes, and has fulfilled its early promise; it is not uncommon now to make 25 or 30 runs without renewal of the insulation. In fact, manipulation of the 30,000 apparatus has now become nearly as easy and as much a matter of routine as was formerly the manipulation of the 120,000 apparatus.

EXPERIMENTAL METHOD, CORRECTIONS, AND METHOD OF CALCULATION

The piezometer assembled inside the 30,000 apparatus ready for a run is shown in Figure 2. The piezometer is filled initially tightly with its charge by squeezing the pistons together in a vise. The amount of charge is determined from a measurement of the over-all length and the known length of the pistons. The amount of charge thus determined is corrected for the volume of the packing rings, which is obtained from their weight. The cross section of the piezometer is given accurately enough in terms of the diameter of the pistons. At first the section was determined by weighing the amount of mercury required to fill it, intending to follow up these measurements at intervals to check for permanent distortion. This more elaborate method proved unnecessary, however, but would have been necessary if the piezometer had been made of steel.

All of the contents of the 30,000 cylinder were inserted into it together in a single assembly. It will be seen from the diagram that the thrust is not transmitted directly to the pistons of the piezometer from the piston of the 30,000 apparatus, but there are several intermediate members. The use of all these intermediate members need not be described here in detail, some of them being atavistic survivals from former work. The principal of these members is a long rod of carbonyl sliding concentrically within a steel tube within which the piezometer is

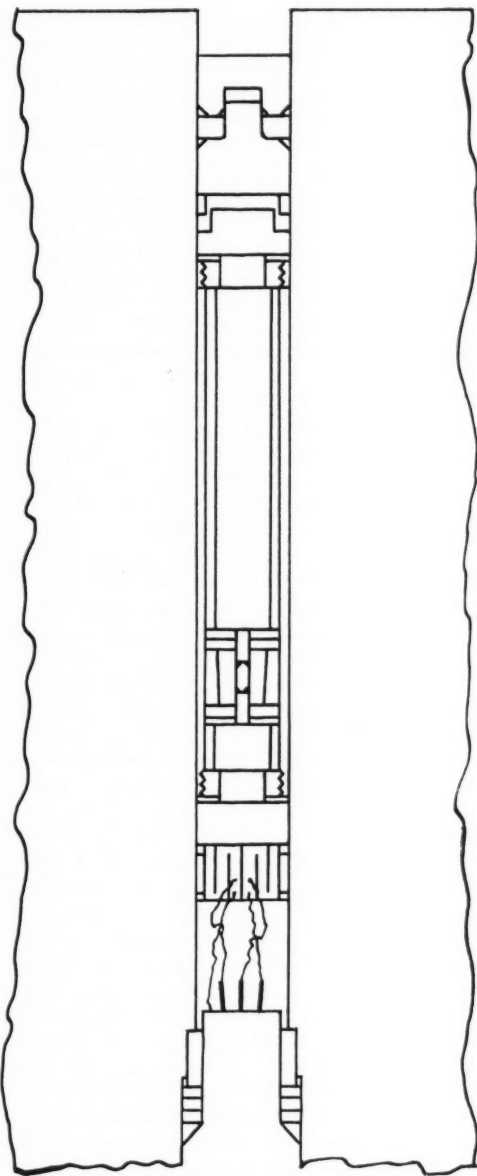


FIG. 2. General assembly; the piezometer within the cylinder in which the supporting pressure is generated.

also mounted. This carboloy compression member and the steel tube play an important part. While the confining pressure of 25,000 is being built up, the contents of the piezometer are of course being compressed, because they are com-

pletely bathed in the confining liquid. Because of the differential compressibility of the piezometer and its contents this means that when 25,000 is reached the charge of the piezometer no longer tightly fills it, but is separated from it by an annular film of liquid. When pressure is now increased in the piezometer beyond 25,000 a capricious amount of this annular film of liquid may be trapped between the charge and the walls, resulting in a spurious and too large an apparent compression. The effect is avoided by maintaining the pressure in the charge of the piezometer during the building up of the confining pressure always greater than the pressure in the confining liquid. How this is done is sufficiently indicated by the diagram. The piezometer is mounted inside a steel tube with screwed-in end plugs, and the balance of the interior of the tube is occupied with carboloy, which comes up tightly against the screw plugs. When confining pressure rises, the steel tube shortens more than the carboloy filler because of differential compression, with the result that the pistons are driven into the piezometer and the pressure on the charge kept greater than the pressure in the liquid, which therefore does not enter between charge and the walls. The result of this arrangement is that the first effect of applying thrust to the pistons of the piezometer by the piston of the 30,000 apparatus is to transfer strain from the walls of the steel tube to the compressometer, so that the displacements do not begin truly to correspond to compression of the contents of the piezometer until a pressure of 30,000 or 35,000 is reached. Before this arrangement was adopted many irregularities were found. If the charge is of unusually high compressibility, a tube of some more compressible substance than steel may be used, and in fact tubes of brass and of aluminum were used in the preliminary work. However, these did not prove to be necessary for the materials of this paper, although it may be desirable to return to them when measuring the more compressible salts.

The 30,000 apparatus, after assembly, is filled with iso-pentane as usual. The requisite amount of liquid so that the piston will make up on the piston of the piezometer at the requisite pressure has to be determined by trial. The amount of liquid was controlled by first filling the 30,000 apparatus and then expelling the superfluous liquid with a moderately tightly fitting plunger pushed in to a mark set by a screw stop. It was desirable to control the setting of this plunger to

0.010 inch. When working to such narrow tolerances the importance of freedom from leak is evident; this work would not have been possible unless practically complete freedom from leak had been attained.

After assembly, pressure is increased in the regular way by advancing the 30,000 piston. Pressure is measured on the manganin gauge. Simultaneously the resistance of the compressometer changes because of the increase of hydrostatic pressure to which it is exposed. This change of resistance is measured also, and a running plot made of the change of resistance of the compressometer against the change of resistance of the manganin gauge. In the range of pressures involved one resistance is a linear function of the other. When the 30,000 piston makes up on the piezometer, additional compressive stress is thrown on the compressometer, and its change of resistance deviates from the former direction because of the added effect of the one-sided compression. The running plot shows this deviation, and from now on manipulations are controlled by the running plot. Pressure is increased on the contents of the piezometer in steps of about 10,000 to the maximum and then decreased in similar steps.

The sensitivity of the galvanometer and other parts of the electrical set-up was such that settings could be made certainly to 0.1 mm. of bridge wire; readings of one resistance against the other were smooth to this amount. During the change of compressive stress on the compressometer its change of resistance arising from compressive stress was about twice as great as that arising from change of pressure in the confining liquid. The compressive stress was therefore determinable with an accuracy limited only by the sensitivity of the readings; at 100,000 this amounted to about one part in 150.

On release of pressure the pistons were measured for permanent set, and any such set applied as a constant correction to the displacement at the maximum pressure and all the subsequent displacements with decreasing pressure. Sometimes, if the reading next below the highest with increasing pressure was too near the highest reading, the effect of set could be detected there also, but as there was no way of knowing its exact amount, this reading had to be then disregarded.

Along with the electrical readings the position of the piston of the 30,000 apparatus was measured. After the piston makes up on the piezome-

ter this gives, except for distortions in various parts of the apparatus, also the displacement of the piezometer piston, and thus eventually gives the compression. The displacement was measured with a jewelled Ames indicator, graduated to 0.0001 inch and allowing estimations to 0.00001 inch, attached to a point near the head of the carboloy piston of the 30,000 apparatus and the upper end of the 30,000 cylinder. The readings of this gauge were very smooth and satisfactory in every way. This gauge permits a fine control of the motion of the piston, which is very necessary when it is considered that the total motion of the piston of the piezometer from 25,000 to 100,000 may be as little as 0.020 inch. Positive control of the settings of the pistons proved to be feasible to a fraction of 0.001 inch.

All readings were made at room temperature, which averaged about 23°, without any attempt at control by a temperature bath, which would have been inconveniently cumbersome. If temperature drifts during a run, the zero resistance of the compressometer drifts also, and the extrapolated difference between the pure hydrostatic effect and the total effect is in error. Correction was made for drift by reading the temperature of the press at intervals during a run, which occupied on the average about two hours, by a thermometer inserted in a brass block soldered to a massive part of the apparatus. The total drift was always less than a degree Centigrade, and usually only a few tenths. The maximum correction for drift in any of the runs was equal to 0.8 mm. displacement of the slide wire setting, which means less than 5% on the differential reading of the compressometer which gives the force on the 100,000 piston.

The compressometer naturally has to be calibrated. At atmospheric pressure this offers no difficulty, and was simply accomplished in a small hydraulic press in which pressure was controlled with a dead weight gauge. The pure hydrostatic pressure coefficient obviously enters the results, but this can be determined *in situ* for every run from the readings before the piston makes up. The values so found were always consistent with each other. The difficulty is in finding the compression coefficient under hydrostatic pressure, for it would not be safe to assume that the compression coefficient is the same under 25,000 kg/cm² as it is at atmospheric pressure. Obviously a method of doing this "in principle" is to get the force on the compressometer from the excess force on the large piston of the 30,000

press when the compressometer is in action over that required to produce the same pressure in the liquid without the compressometer. The practical difficulties are the smallness of the excess force and the irregularities introduced by friction. The cross section of the 30,000 piston is 64 times that of the 100,000 piston, and the sensitiveness of the measurement of the high pressure in terms of the pressure driving the plunger of the large press correspondingly less than the sensitivity of measurement of the lower pressure, and it is known that this method is not satisfactory for the latter. However, it appeared that various refinements were possible, and I made some attempts to get a direct measurement by making a relatively insensitive compressometer so that during the calibration it could be stressed to a considerably higher compression than during the final measurements. These measurements were too irregular to be satisfactory, but did suffice to give a rough value for the effect. It appeared that frictional irregularity would probably always be too great to permit satisfactory individual readings, and the conclusion was finally reached to smother these irregularities by a great number of different set-ups. For this purpose it was fortunate that the pressure gauge with which the pressure driving the large piston of the 30,000 apparatus was measured was of an unusual degree of mechanical perfection. This gauge was of the Bourdon type, made 40 years ago by the Société Genevoise. It has a range of 1000 kg/cm^2 , and has very seldom been used above 700. It was one which I had inherited from the late Professor T. W. Richards. It is graduated to 10 kg/cm^2 , but the perfection of its multiplying mechanism is such that Professor Richards had attached at various fiducial points auxiliary scales graduated to 1 kg/cm^2 , and was accustomed to make his readings with a glass to 0.1 kg/cm^2 . I did not attempt any such refinements, but contented myself with readings to 1 kg/cm^2 . The readings appear to be consistent at least to this limit, which is much better than I have been able to do with any gauge made in this country. The gauge has been calibrated from time to time against a dead weight gauge, and is satisfactorily constant.

Knowing the approximate value of the pressure coefficient of the compression coefficient, so that pressures could be kept within the desired range, the more exact value was found from a multiplicity of readings. Regular runs were made, and a record kept of all the changes of resistance and also of the pressure as recorded on

the Geneva gauge. From these many readings, the normal reading of the Geneva gauge against pressure in the iso-pentane of the 30,000 apparatus was determined, and then the excess reading when the piston was made up on the 100,000 piezometer. The final results are from 16 complete runs, involving more than 300 points. Readings with increasing pressure and with decreasing pressure were treated separately to better eliminate friction. In getting the final grand average the results were weighted according to the absolute magnitude of the effect. The friction on the average was surprisingly small, being only 3.7%, which means that a reading with increasing pressure differs by 7.5% from a reading with decreasing pressure. This frictional effect is only that contributed by the two larger pistons; it does not include the friction on the small piston of the 100,000 apparatus, which naturally was much larger and also more irregular. Within the limits of error the change of resistance is linear in the compressive stress at any single confining pressure. The pressure coefficient due to the confining pressure is such that at 25,000 the compression coefficient is 15% less than at atmospheric pressure. There was no indication that this 15% is not linear in the confining pressure, and it was so assumed. If no correction had been applied for this effect, pressures would have been obtained at 100,000 15% too low. Since the confining pressure changes with increase of pressure in the 100,000 piezometer, the correction changes also, with the result that the compressive force on the compressometer is not a linear function of the deviation of the measured change of resistance extrapolated from the hydrostatic pressure part of the curve. Correction was made in the following for this deviation; the maximum error from this effect is about 4%. If the correction is not applied the pressures toward the maximum get too low, with the result that the compressibility at the high pressures would not drop off enough. The second compressometer, used after the first was fractured, was directly calibrated only at atmospheric pressure, assuming the same pressure coefficient of the compression coefficient. This seemed justified because the two compressometers were made from contiguous lengths of the same bar of steel, and their heat treatments were the same.

After the run was completed and the apparatus disassembled, the over-all length of the piezometer with pistons was again measured and also the dimensions of the pistons. Correction was ap-

plied for any permanent change of length as already described. The over-all length then afforded a check on permanent change of internal diameter of the piezometer; this practically never was found. The next step in working up the results was to convert the compressometer excess resistances, obtained by simple linear graphical extrapolation from a plot five times the scale of the slide wire readings, into actual pressures on the contents of the piezometer. This involves the cross section, and this demands a correction for change of cross section. This correction was calculated by conventional methods of the theory of elasticity, and need not be described in detail. Three different effects had to be taken into account: the effect of the confining pressure, the effect of the differential compressibility of the steel jacket shrunk on the carboly core, and the effect of the internal pressure in the carboly. The elastic constants of carboly are approximately three times those of steel. The fundamental numerical value was taken as the value of Young's modulus which had been measured by Dr. Dennison Bancroft by a dynamic method on a number of different samples of grade no. 905 carboly and found to average 64.5×10^{11} , Abs. C. G. S. units, with deviations seldom as much as one per cent. The other constants of carboly were assumed to bear the same ratio to its Young's modulus as the other constants of steel bear to Young's modulus of steel. This assumption had been approximately checked by a direct measurement by me of Poisson's ratio for the same grade of carboly. There is some evidence that the assumption may not be as good for other grades of carboly, but the difference is probably unimportant. The correction calculated in this way is an increase of cross section of 3.2% at an internal pressure of 100,000 kg/cm² and a confining pressure of 25,000. This correction changes by 0.1% for a change of 5,000 in the confining pressure, an effect so small that it was neglected. At the working end of the pistons the correction is only one half as great. It was this correction that was applied in reducing compressometer readings to pressures. The full correction of 3.2% has to be applied at a later stage in reducing the observations.

In evaluating the corrections for distortion, two effects were considered which were neglected in my previous work to 50,000. In the first place, the ratio of diameter of piezometer to its length is only 3, so that it is to be considered whether end effects do not enter into the change

of cross section, which was calculated from the simple formulas for infinitely long cylinders. In my previous work I had tried to convince myself by a crude graphical analysis that such effects were probably not important. Very recently, however, Dean Westergaard⁶ has made a mathematical analysis of the problem which permits a much more satisfactory conclusion. It appears that the effect is not large enough to introduce appreciable error. Another consideration is that the strains are getting so large at these high stresses that it is conceivable that the ordinary theory of infinitesimal strains is not good enough, but should be replaced by the theory of finite strains which has recently been put on a satisfactory basis by Murnaghan.⁷ It appears that in the case of steel this effect would have to be considered. Professor Murnaghan was kind enough to make the calculations, and found that for a cylinder with infinitely thick walls stressed by internal pressure to such a value that the classical theory of infinitesimal strains would indicate an increase of cross section of 10%, the more accurate theory of finite strains would give a result 8% smaller. This effect is proportional to the magnitude of the strain. The correction calculated above for carboly would therefore be in error because of this effect by less than 3% of itself. Since 3% of a 3.2% correction is only 0.1% the effect need not be considered in this work.

The true pressures having been obtained, the next step was to plot the piston displacements against pressure, taking as the zero the displacement at which the piston first makes up. Smooth curves were then drawn through these points, one curve for increasing pressure and one for decreasing. The lowest point was likely to be off, because of the effect of the steel tube, as already explained, and was often discarded. Also the highest points on the decreasing curve had to be neglected, because for them the motion was not yet great enough to completely reverse the frictional effects. The mean curve was then drawn through the two curves, taking the mean pressures at constant displacement. It has already been explained in one of my papers dealing with measurements to 50,000 that this gives a better correction for the effect of friction than the mean displacement at constant pressure. From this mean curve the displacements at even pressure intervals were tabulated; the initial pressure was 25,000 (the average initial confining pressure in all the experiments), the next 30,000,

and then 40,000 and at 10,000 intervals to 100,000.

From these tabulated displacements were then subtracted the displacements which had been obtained by an exactly similar procedure for the comparison runs with gold, which was chosen as the standard substance because of its low compressibility and mechanical softness, as already described. Four piezometers were used in this work and six calibrating runs were made with gold, two with each of the two piezometers most extensively used. All six calibrating runs agreed within 5% of themselves; part of the difference is to be ascribed to slight differences in the dimensions. The consistency of these calibrations was gratifying and better than I had expected. It does not appear that there is any significant difference in the different grades of carboloy, and the corrections calculated for grade no. 905 were applied throughout. There have been measurements of the constants of the various grades which support this procedure. The total displacement from 25,000 to 100,000 for the calibrating runs with gold was 0.020 inch. Of this total 0.006 is contributed by the compression of the gold, 0.005 by the change of cross section of the piezometer, and the balance by the distortion of the various parts of the apparatus.

The differential displacements give the differential compression of the material under examination and gold, except for various corrections. In the first place, this statement assumes that the distortions of the rest of the apparatus are the same for the run with gold and the other material. This is not quite true, the distortions of the apparatus depend both on the hydrostatic pressure prevailing in the fluid of the 30,000 apparatus, and the compressive force with which the pistons make up. The confining pressure in the run with gold rises at a slower rate than in the run with the material in question because of the smaller compressibility of gold, and a correction has to be applied for the lack of equality of the confining pressure in the two runs. This correction was determined by various dummy runs with the piezometer or other parts of the apparatus replaced by carboloy, and need not be described in further detail. The correction so determined averaged about 6% of the differential displacement.

Further reduction of the results to obtain finally the fractional change of volume in terms of the volume at atmospheric pressure as unity was sufficiently straightforward. A correction

is involved approximately additively for the assumed compression of gold as a function of pressure, an approximately multiplicative correction for the full cross sectional distortion amounting at the maximum to 3.2%, and an approximately additive correction proportional to the product of the fractional distortion of the cross section and the difference between the initial volumes of the material in question and the gold of the calibrating run. This latter term is obviously small. The compressions assumed for the gold at the high pressures were computed by Murnaghan's formula with one constant combined with my experimental determination up to 12,000 using the corrected second degree term obtained from my measurements up to 30,000. The values thus assumed for gold were: 0.0133, 0.0255, and 0.0483 at 25,000, 50,000, and 100,000 kg/cm² respectively.

Most important of all the data necessary for the final reduction is the compression at 25,000 of the substance, since obviously all these measurements are from a zero of 25,000. This value was usually obtainable from preceding work.

Two runs with two fillings of the apparatus, often with different piezometers, were made for every substance but one. The final results are the average of the two runs, each computed as just described. This average was finally subjected to a smoothing for first differences; the final smoothing usually did not affect the last significant figures by more than one.

DETAILED RESULTS

There follows now the detailed presentation of results. These are all collected into a single table, which has already been presented in the *Physical Review*.⁸ The arrangement is by columns in the periodic table.

The four alkali metals were measured by a different and less accurate procedure than all the others. The lower accuracy of the results for these metals is unfortunate, because it is just these which are simplest from a theoretical point of view and therefore most amenable to theoretical treatment. The necessity for a different procedure arose from the presumptive chemical action between the alkali metals and the walls of the piezometer. Such action was perhaps not conclusively established. It had been definitely established in my former work to 50,000 that there is such action with steel. On the first attempt in the present series of experiments to use

TABLE I
COMPRESSION OF SEVENTEEN ELEMENTS

Pressure Kg/cm ²	Li	Na	K	Rb	Cs	Sr	Ba	Zn	Cd	In	Tl	Sn	As	Sb	Bi	Se	Te
10,000	0.074	0.117	0.183	0.233	0.058	0.075	0.086 (d)	0.016	0.022	0.023	0.023	0.018	0.047	0.025	0.028	0.089	0.045
20,000	.125	.182	.268	.316	.103	.122 (b)	.159	.031	.042	.045	.043	.034	.083	.047	.052 (h)	.149	.079
30,000	.164	.232	.329	.371	.139	.172 (b)	.211	.046	.060	.064	.061	.049	.109	.066	.158 (h)	.187	.111
40,000	.201	.273	.377	.419	.168	.209	.253	.061	.076	.081	.079(f)	.064	.132	.083	.174 (i)	.208	.138 (l)
50,000	.237	.310	.419	.462	.195	.239	.288	.075	.091	.097	.103	.077	.152	.098	.192 (i)	.227	.214 (l)
60,000	.272	.343	.457	.501	.220	.266 (a)	.318(e)	.088	.104	.112	.119	.091	.171	.112	.205 (j)	.243	.225
70,000	.305	.372	.492	.539	.252 (a)	.298 (e)	.361	.100	.116	.126	.132	.103	.188	.124	.222 (j)	.258	.234(m)
80,000	.336	.397	.522	.575	.268	.317	.382	.111	.127	.140	.145	.114	.204	.136 (g)	.232	.271	.250
90,000	.366	.419	.549	.608	.284	.335	.402	.122	.138	.153	.157	.125	.219	.185 (g)	.240(k)	.283	.258
100,000	.394	.440	.573	.638	.298	.352	.420	.132	.148	.165	.169	.136	.233	.197	.261	.295	.267

(a) Transition at 64,000. Compressions: 0.229 and 0.242.

(b) Transition at 25,000. Compressions: .143 and .152.

(c) Transition at 65,000. Compressions: .279 and .287.

(d) Transition at 17,000. Compressions: .135 and .141.

(e) Transition at 60,000. Compressions: .318 and .337.

(f) Transition at 40,000. Compressions: .079 and .086.

(g) Transition at 85,000. Compressions: 0.142 and 0.179.

(h) Two transitions at 25,000. Extreme Compressions: .064 and .150.

(i) Transition at 45,000. Compressions: .180 and .186.

(j) Transition at 65,000. Compressions: .211 and .216.

(k) Transition at 90,000. Compressions: .240 and .252.

(l) Transition at 45,000. Compressions: .152 and .207.

(m) Transition at 70,000. Compressions: .224 and .241.

the regular method with lithium the piezometer ruptured before reaching the maximum pressure. The probability of chemical action seemed too great to risk the rupture of other piezometers. These alkali metals were therefore protected from direct contact with the walls of the carboly piezometer in the subsequent work by being enclosed in a capsule of copper. Because of the great distortion, the capsule has to be made with heavy walls. The total volume of copper was twice that of the enclosed alkali metal. Even with this amount of copper the walls were thinned down to practically nothing in some places after a single excursion to the maximum pressure, so that it would not have been possible to use a smaller amount of copper in spite of its desirability from the point of view of accuracy. The capsule was sealed by spinning over the open end in the lathe, or in some cases by inserting a plug in the open end and giving a precompression in the piezometer. The amounts of copper and alkali metal were determined at first by weighing. The weight of the copper was of the order of 0.050 gm, and that of the alkali metal varied from 0.002 to 0.004 gm. This latter is so small as not to give the total amount with the desired accuracy, so that for the final calculations the amount of alkali metal was taken from the volume as given by the over-all length of the piezometer with pistons, assuming that the part of the volume occupied by the copper was given with sufficient accuracy by its weight because of its greater mass. The dimensions of the charge could be

determined from the over-all length to about one part in 200. The volume of the alkali found in this way agreed within 10% with the less accurate volume given by the weighing.

The result of the measurements with the capsules is a compression contributed jointly by copper and alkali. To isolate the contribution of the alkali it is necessary to know the compression of copper. This is much smaller than that of the alkali, and I assumed that it would be given with sufficient accuracy by an extrapolation made by an application of Murnaghan's one constant formula to my values up to 12000, properly corrected, as in the case of gold. The values thus assumed for the compression of copper were: 0.0170, 0.0325, and 0.0608 at 25,000, 50,000, and 100,000 respectively. The contribution of the copper to the total compression varied from 15 to 20%.

This contribution by the copper is so small, because of the very high compressibility of the alkalies, that the accuracy would not be seriously limited by this factor. The limitation of accuracy arises from the great friction exerted by the copper, which is much harder than most of the other materials measured here. The uncertainty from this effect is particularly serious at the lower end of the curves. The result was that the agreement with my previous results in the common range between 25,000 and 50,000 was poorer than for the other materials. I believe the previous results are preferable, because the previous method should give its best results just for these

metals because of their high compressibility. In view of this, the present results were corrected in the following way. The displacement at 50,000 was calculated which would have been necessary to make the present results agree with the former ones. The difference between this displacement and the actually observed one was then applied as an additive correction to all the observed displacements up to 100,000. The regular calculations applied to these displacements then gave a curve of compression which was continuous with the former curve of compression at 50,000, but which has a break in direction at 50,000. The final result was obtained by smoothing graphically this break in direction across 50,000. The results tabulated in the following are therefore controlled in the main by the former results below 50,000, but diverge somewhat from them, particularly toward the upper end of the former range, near 50,000. In addition to this special dependence of the results for the alkali metals on the previous measurements, the compressions at 25,000 and below tabulated in the following are lifted straight from previous work, as for all the other substances.

The magnitude of these adjustments is indicated by the following figures. For lithium the compression at 50,000 given by these measurements before application of any corrections was 0.263, as compared with the figure 0.233 from previous work; for sodium the corresponding figures are 0.371 and 0.306; for potassium 0.462 and 0.416; and for rubidium 0.520 and 0.449. The new work differs consistently from the old in giving higher compressions over the entire range. There is nothing inherently improbable, however, in the new values. Evidence as to internal consistency is given by a graphical examination. The decrease of rate of compression with rise of pressure must be such that the volume approaches zero asymptotically at infinite pressure. The graphs make such an asymptote appear reasonable. This requirement says more than might appear to on the surface, because with this particular arrangement, in which part of the compression is contributed by the copper, it is quite conceivable that values might have been obtained for the over-all compression which would appear reasonable from the point of view of the simpler procedure for the other substances, but which on calculation should yield a negative volume for the contribution of the alkali part at the highest pressures.

The only particular in which the results have

a certain degree of antecedent improbability from the graphical point of view is for sodium; the compression of this seems to flatten out too rapidly at the highest pressures to be in line with the other alkalies.

A slight degree of presumptive evidence as to the accuracy of these results is given by the original single run on lithium before the capsule was used with increasing pressure up to nearly the maximum, where rupture occurred. In this run the material completely filled the piezometer, and pressure was transmitted directly to the carbonyl by it. The compression at 100,000 given by this single run, which is too low because of friction, which could not be determined because there were no readings with decreasing pressure, was 0.348 against 0.394 listed above from the measurements with the copper capsule. No adjustments were applied to the figure 0.348 in the direction of agreement with former results.

There is no intrinsic reason why the measurements should not be made on caesium as well as on the four given. The apparatus was set up with caesium and measurements made up to the maximum, when a major rupture occurred, one of the supporting rings of the 30,000 apparatus which had been in use continually for several years, and the repair has not yet been effected. This single run permits only the statement that the compression of caesium remains greater than that of rubidium by something of the order of 15%.

The alkali metals were of adequate purity and were from my stock. They are the same as used in my previously reported measurements to 50,000.

One of the questions suggested by these measurements is whether the other alkali metals show polymorphic changes in the new range analogous to the transition of caesium at 23,000.⁹ None were found. The volume change of the transition of caesium is 0.006. This is small, but several fold larger than is easily detectable by this method under normal conditions. However, it is not entirely ruled out that a transition of this magnitude might have been so smeared out by the friction of the copper as to escape detection.

As usual, the figures of the table are the average of two independent runs. Some additional indication as to the accuracy is given by the agreement of the two runs. For lithium, the compressions at 100,000 of the two runs differed by 1.9% of themselves, or 0.95% from the mean; for sodium the difference from the mean was 1.2%, for po-

tassium the difference from the mean was 1.9% and for rubidium 6.2%. It is curious that the disagreement increases as the absolute compressibility increases.

The three alkali earth metals, calcium, strontium, and barium, were from the same supply as that used in previous measurements. The piston displacements were larger than for any of the other substances; the displacement for barium at 100,000 was 0.063 inch, more than three times the displacement for gold. These metals are soft and the width of the loop due to friction therefore small; for barium at the top pressure the friction loop was 10,000 kg/cm² wide, which means that rising and falling curves differ 5,000 kg/cm² from the mean, or 5%. Both the softness and the high compressibility of these three substances make for accuracy. For calcium the compressions of the two runs at 100,000 differed 0.9% from the mean. The average compression at 50,000 was 0.190, against 0.204 found previously. The former value was given some weight in selecting the value of the table at 50,000, which is given as 0.195. Calcium was found in the former work to have a transition in the vicinity of 25,000 or 30,000, but the volume change is small and the transition does not run cleanly enough to give good values for the parameters, so that the compressions of the former paper were smoothed right across the transition. Unmistakable evidence of a transition in the same locality was found in this present work also, but since its characteristics were no better than before, the parameters could not be evaluated, and the compressions of the table are smoothed across the transition as before. In addition to the transition already known, a new transition was found at approximately 65,000. This is much more clean cut and definite than the transition at lower pressures. The volume change for the new transition given by the two set-ups was 0.014 and 0.017.

The compressions at 100,000 of the two runs with strontium differed by 0.04% from the mean. At 50,000 the average compressions of these two runs differed by 0.6% from the former value. Strontium has a transition at 25,000, below the range of the present work, whose parameters were previously determined, and a new, small, but well marked transition at 65,000. The transition pressures given in the following for various materials make no great pretense to accuracy; the fact that pressures were usually altered in steps of 10,000 is not favorable to accuracy. The

volume change for the transition given by the two set-ups was identical, 0.007.

The two set-ups with barium gave compressions at 100,000 differing by 3.7% from the mean. The second of these was weighted double in the final result because of greater completeness and regularity of the readings. At 50,000 the compression of these new measurements differs by 0.3% from that previously found. Barium has a well marked transition at 60,000 in addition to the one previously known near 15,000. The two set-ups gave identical values for the volume change of this transition, 0.019.

The next two metals of the table, zinc and cadmium, have compressions so small that the method is becoming less well adapted. The chief interest in measuring them was the possibility of transitions, which might perhaps be anticipated because they are both so strongly anisotropic in their properties under normal conditions. Cadmium is known to have a very small transition at low pressures.¹⁰ The material in both cases was spectroscopically pure; the same stock has been used in previous work, and I owe it to the courtesy of the New Jersey Zinc Co. No new transitions were found. It is to be remembered that the compressions given in the following are average compressions for all directions in the crystal; the linear compressibility in different directions in the crystal varies by a factor of eight. The compressions at 100,000 of the two runs with zinc differed by 1.2% from the mean. There are no previous measurements to 25,000 for the fiducial initial compression. For this I assumed the value 0.038, obtained by an extrapolation of my second degree formula reproducing my results up to 12,000. In this, my recently redetermined value for iron was used, as in all similar cases in this paper. The compressions at 100,000 of the two runs for cadmium differed from the mean by 1.3%. There are no measurements of the compression of cadmium above 2,000. The reason for this is that previous measurements had been of the linear compressibility for different directions in the single crystal, and at 2,000 there is a small transition which changes the single crystal into a crystalline aggregate, and the method becomes inapplicable. The best that I could do for the fiducial compression of cadmium at 25,000 was to assume that the compressibility of cadmium retains over the pressure range up to 25,000 its initial ratio to that of zinc. This assumption is perhaps not too implausible in view of the very small volume change of the transition, and the

fact that there are many cases where polymorphic change occurs with small change in compressibility. The fiducial compressibility at 25,000 obtained in this way was 0.051. Its ratio to that of zinc is 1.35. At 100,000 the ratio of the compression of cadmium to that of zinc is 1.12. It would appear that probably the assumption of a constant ratio of the compressions of cadmium to zinc is at best rough even for the range up to 25,000.

Indium, the next metal of the table, was tried because of its softness, because it is compressible enough to come within the range of the method, and because its unusual crystal system, tetragonal, suggests the possibility of a transition. No transition was found. The material was the same as that used in my previous work to 50,000. Only one complete run was made with this material. The piezometer fractured at the maximum pressure on the second set-up, as has already been described. There was no perceptible difference between the parts of the runs with increasing pressure on the two set-ups, and there is no reason to expect that the accuracy of the final result differs materially from that of other substances. At 50,000 the compression of this new work differs by 3% from my former value. The former measurements were made with an early form of apparatus and were described as "rough." The new result is doubtless to be preferred.

Thallium, the next metal, is one of the more compressible metals and is known to have a well marked transition near 40,000. The same material was used as before, some highly purified material which I had inherited from the late Professor T. W. Richards. No new transition was found. For some unknown reason one of the two set-ups gave values below the transition at 40,000 which were impossibly high, as could be seen by extrapolating them graphically back to zero. Hence only the other run was used in making up the values below 40,000. Above 40,000 the differential compressions of the two runs were averaged. At 100,000 the two compressions given in this way differed by 3.6% from the mean. Again a well marked transition was found near 40,000. No very good values were obtained for the volume change, which was also the case in the previous work. One run gave 0.011 and the other 0.007, against the previous value 0.005. The value given in the table is 0.007, taking the one of the two values which is closest to the previous one. Evidently there is considerable uncertainty here. There are no previous measure-

ments of the compressibility of thallium above the uncertain ones of Richards up to only 500 kg/cm². The reason that I have not attempted it myself to high pressures is that thallium is non-cubic and I have been waiting for a chance to make the single crystals. For the fiducial compression at 25,000 I assumed out of whole cloth that it is the mean of lead, 0.050, and indium, 0.054, this giving 0.052. The compressions below 25,000 listed in the table were obtained from this and the values at higher pressures by graphical extrapolation.

Tin, the next metal, is, except for zinc, the least compressible of the materials measured here. It is non-cubic, and therefore is a candidate for transition. None was found, however. The material was Kahlbaum "K" material obtained a number of years ago, which had been further purified by being made up into single crystals. The compressions at 100,000 of the two set-ups differ by 2.1% from the mean. At 50,000 the average compression of the two runs differed by 6.5% from the former value. However, the former value was one of my first measurements, recognized as "rough," and was probably among the least accurate of them. The new values indicate a smaller compressibility than the former rough ones. I think there is no doubt but that the new ones are to be preferred, and in the table the values at the low pressure end are adjusted to make smooth connection with the new values, rather than using the old values as usual.

Arsenic, the next element, is highly non-isotropic, and transitions might be expected both because of its occurrence in the same column of the periodic table with bismuth, and because of the known abnormalities at low pressures.¹¹ None were found, however. The material was originally from Kahlbaum, but it had been further purified by several distillations and by formation into single crystals. Purification of the original material is particularly necessary for arsenic, because it contains in the dissolved condition a large amount of its own oxide. The possibility of producing single crystals affords a sensitive test of its final purity. Only a single run was made with this material, the piezometer fracturing on the next filling, with gold. I feared the result of chemical attack and so did not risk other runs. There is therefore no internal evidence from which the accuracy of the final result may be estimated. It is probable, however, that it is less than usual. In spite of its high compressi-

bility, arsenic is perhaps the hardest of the materials measured here, and the frictional hysteresis was unusually great. The only previous measurements of the compressibility are by Richards in the range up to 500 kg/cm². Over this range it is 2.6 times more compressible than zinc. I assumed that this ratio is maintained up to 25,000, giving a fiducial compression at 25,000 of 0.097. The listings in the table at lower pressures were obtained by graphical extrapolation.

Antimony has long been a candidate for a transition because its crystal structure is identical with that of bismuth. It is therefore gratifying that a transition was found, although at an unexpectedly high pressure, 85,000, against 25,000 for bismuth. The volume change is so large, nearly 4%, as to suggest that this is actually the same structural transition as the first transition of bismuth. The volume change was so large that settings could be made on the actual equilibrium with both phases present, the only one of the materials of this paper for which this was possible. The material was originally "K" material from Kahlbaum, made up into single crystals. At 100,000 the two compressions differed by 1.5% from the mean. At 50,000 the mean of the two present compressions differed by 1% from the former value. For the volume change at the transition the two runs gave 0.035 and 0.039.

Bismuth was an obvious candidate for examination because of its many abnormalities at atmospheric pressure and because it is known to have three transitions below 50,000.¹² Two new transitions were found, which means six modifications in all, making bismuth the most versatile known metal. There is a rather close parallel between the transition patterns for bismuth and for water; it will be recalled that both bismuth and water freeze with increase of volume, and that the melting curve initially drops with increasing pressure. The new transitions of bismuth take place at 65,000 and 90,000; the latter has the larger change of volume. The previous nomenclature will be extended, and the modification stable between 65,000 and 90,000 called bismuth V, and the one stable above 90,000 bismuth VI. The transition from IV to V is suppressed with increasing pressure, IV passing directly to VI. But with decreasing pressure the transition is resolved. A similar situation occurs under proper conditions with water.

The material was from my single crystal stock, which had been purified by a double electrolytic

deposition. At 100,000 the compressions of the two set-ups differed by 4% from the mean, a greater discrepancy than usual. The individual phases of bismuth have a comparatively small compressibility, the larger part of the changes of volume being contributed by the phase changes, so that less accuracy than usual is to be expected for the compressions of the pure phases. The present compression between 25,000 and 40,000 is 40% greater than the former value; this means, however, a much smaller discrepancy on the total change of volume. For the previously known transition at 45,000 the volume changes 0.005 and 0.007 were found, against the former value 0.0024. The present value is certainly to be preferred because the transition is so near to the end of the former range that it may not have run to completion. For the new transition at 65,000 the two runs gave volume changes of 0.005 and 0.006. At the upper transition at 90,000 the two values were 0.009 and 0.015; this is so near the end of the range that accuracy is reduced. The compressions given in the table between 25,000 and 40,000 were based almost entirely on the new work, disregarding the former. The table lumps together at 25,000 the two transitions I-II and II-III; the transition parameters for these separately are given in the preceding papers.

Selenium is obviously a candidate for a transition because of the known multiplicity of forms at atmospheric pressure. The material was the same as in my previous measurements to 50,000, which I owe to the courtesy of the American Smelting and Refining Co. who had specially purified it. Three set-ups were made with this material; the second set-up gave points with increasing pressure only, the run being terminated by an explosion at the maximum pressure. Selenium is known to be in a state of incomplete internal equilibrium under normal conditions, and this was confirmed by the failure of the measurements at high pressure to be reproducible. The material originally placed in the piezometer was a shiny black glass, obtained by melting of the original black powder in a pyrex tube with a bunsen burner until evolution of gas had ceased, and slow cooling. The first run gave a curve with a distinct break in direction at 63,000. The second run, increasing pressure only, gave larger changes of volume than the first, and also the break in direction at 63,000. The third run was not made with virgin material, as had been the first two, but was with mostly the material from the second run which had been exposed to 100,000,

to which a small amount of virgin material was added to make up the quantity. The compression was markedly smaller than that of the first run, at 100,000 being 0.295 against 0.335. The same break in direction near 60,000 was found with increasing pressure as with the first two, but much less in magnitude, and the break had disappeared with decreasing pressure. It would appear that some permanent change is produced by the application of pressure, although it is too small to show up as a measurable change of volume. Since the compressions between 25,000 and 50,000 of the third run agreed with the previous measurements¹³ to better than one per cent, it is the results of the third run which are given in the table. Above 50,000 the present results are a smooth continuation of the previous ones. Attention should be given to the sharp break in direction in the neighborhood of 25,000 found in the previous work, and doubtless connected in some way with the glassy condition. The character of the compression curve of selenium is unlike that of all the other substances of this paper, being characterized by an initial steep rise and then an unusually rapid falling off at the high pressures.

Tellurium has already been investigated¹⁴ to 50,000; at room temperature it has one transition just above 40,000. One new transition was found in the new range, at 70,000, with a volume change only one eighth as large. The material was the same as that used in the previous measurements, purified by the Research Department of the Raritan Copper Works some 17 years ago. The agreement between the two set-ups was not as good as usual in spite of the fact that the friction was no more than usual. At 100,000 the compressions differed from the mean by 4.3%. The volume changes at the low pressure transition were 0.049 and 0.061 against the former value 0.0044. Both the new values are higher than the former one; the new values are doubtless to be preferred because the transition comes so near the end of the previous range that it may not have run to completion. For the high pressure transition the two runs gave for the change of volume 0.004 and 0.010; the mean was used in the table. There is a striking drop in the compressibility on passing through the low pressure transition; this could not be established by the former measurements because the transition is too near the end of the range. On the other hand, there is not much change in compressibility on passing through the high pressure transition.

In addition to the materials listed in the table a great many applications of pressure were made in the preliminary work to lead and to NaCl. It may be stated that neither of these substances has a transition up to 100,000, at least of a magnitude comparable with those listed here.

DISCUSSION

Many of the important points have already been mentioned in the detailed presentation of data. The general shape of the curves of compression against pressure is of interest. This is given crudely by the ratio of the compression at 100,000 to that at 50,000 and is shown in Table II.

TABLE II

Substance	$\frac{\Delta V_{100,000}}{\Delta V_{50,000}}$	$\frac{\Delta V_{50,000}}{\Delta V_{25,000}}$
Li	1.67	1.63
Na	1.42	1.49
K	1.36 ₅	1.39
Rb	1.38	1.34
Zn	1.76	1.95
Cd	1.63	1.78
In	1.70	1.76
Sn	1.76 ₅	1.85
As	1.53	1.57 ₅
Se	1.30	1.33 ₅

Obviously the ratio has significance only for those substances with no transitions. The ratio of the compression at 100,000 to that at 50,000 is to be compared with the ratio at 50,000 to that at 25,000. The latter should be greater than the former, for obviously if the ratio does not drop with rise of pressure the volume will presently become negative. This expectation is fulfilled in the case of the ten substances for which the ratio has significance because of the absence of transitions, except for lithium and rubidium. In the case of the latter the slight rise in the ratio may possibly be due to error in the low pressure compressions, which are known not to be as accurate as for the other alkali metals. For lithium the absolute values of the volume decrements are small enough so that failure of the condition does not mean the imminence of catastrophe, but it is obvious that there must be some reversal of the trend for lithium at higher pressures. In general, it was a surprise to me that the ratio does not drop more with increasing pressure; this is another way of saying that the compressibility does not drop off with rising pressure as much as I had expected.

The ratios should in general be higher the smaller the absolute values of the compression. That this is true for most substances has been known for a long time¹⁵ in a lower pressure range. However, there are minor exceptions, as shown by the failure of the ratios to lie on a single smooth curve when plotted against the absolute compressions. The accurate fulfillment of any such condition as presupposed in Murnaghan's analysis, for example, would demand a single smooth curve. The most striking exception is, as already mentioned, for selenium.

Another point of interest is the change of compression on passing through a transition. This is given by plotting first differences from the table against pressure. The only cases in which there is any discontinuity in compressibility definitely beyond experimental error are the low pressure transition of tellurium, where the compressibility of the high pressure modification is less than one half that of the low pressure modification, and the transition of calcium, for which the compressibility of the high pressure modification is about two thirds that of the low pressure modification. This is the reverse of the state of affairs that has been found to be generally characteristic of transitions, for in general the compressibility of the high pressure phase is greater than that of the low pressure phase for those transitions investigated over the previous

lower pressure ranges. The differences previously found were usually small, however, and would probably be beyond the error of the present measurements.

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